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Oxo Group Protonation and Silylation of Pentavalent Uranyl Pacman Complexes**

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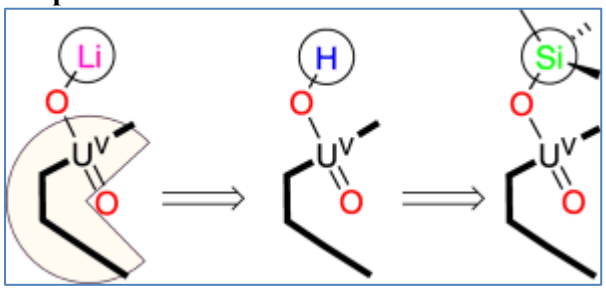
Graphical abstract:



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actinides;oxo functionalization;pentavalent uranyl;schiff-base macrocycle;uranyl hydroxide

Abstract

New bonds for the uranyl - The controlled conversion of one uranyl oxo group to either a covalently-bonded UO-H or UO-Si group is described for pentavalent uranyl ($[UO_2]^+$) Pacman complexes. The unusual oxo-hydroxyl motif is achieved by a protonation reaction and retains the normally unstable U(V) uranyl oxidation state. This product is readily silylated by treatment with a chlorosilane resulting in UO-Si bond formation.

Main text

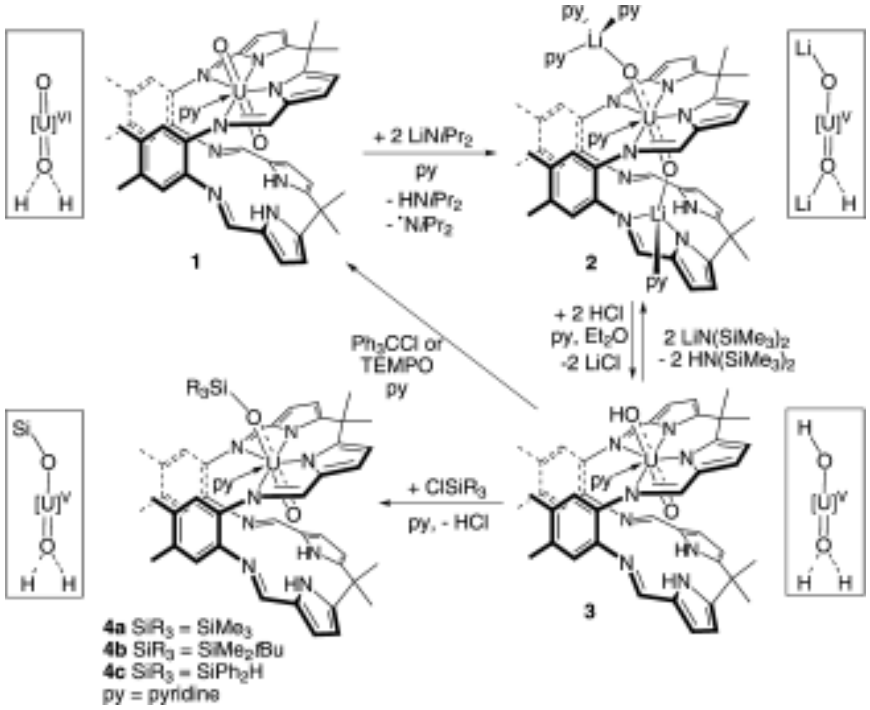
The chemical reactivity of the oxo-group of the uranyl dication, $[UO_2]^{2+}$, the most prevalent aqueous and environmental form of uranium and by far the most chemically inert, has been transformed in recent years.[1, 2] For example, new routes to the singly-reduced, pentavalent uranyl have been developed and have facilitated fascinating new Lewis acid-base interactions between the oxo-groups and alkali metals,[3, 4] boranes,[5-7] transition metals,[8] rare earth metals,[9] and other uranyl cations.[10] In some cases it is evident that oxo-group functionalization can modify the U^{VI}/U^{V} reduction potential such that reduction is facilitated.[3, 6, 7]

While the above cation-cation interactions (CCIs) in $[UO_2]^+$ compounds are becoming increasingly understood, reactions of $[UO_2]^{2+}$ that result in covalent bond formation at one or both oxo groups are extremely rare and at present limited to reductive silylation that forms a UO-Si bond. We showed recently that uranyl Pacman complexes, in which the uranyl oxo groups are in different spatial environments, underwent reduction and oxo-group silylation reactions on treatment with potassium bases and transition metal halides.[11, 12] Subsequently, perfluoroaryl borane-functionalized uranyl complexes have been shown to undergo reductive silylation reactions with tertiary silanes,[6] while the direct reaction of uranyl complexes with Me_3SiI results in U^{V} and U^{IV} oxo-silylated complexes.[13] Furthermore, complete de-oxygenation of $[UO_2]^{2+}$ can be realized by reaction with trimethylsilyl halides, forming U^{IV} halides and $(Me_3Si)_2O$, presumably via a reduced, oxo-silylated intermediate.[14] These reactions can be contrasted to those of the photochemically-generated $*[UO_2]^{2+}$ ion which, in aqueous solution, can abstract an H-atom from alkanes and arenes to form carbon radicals and transient $[UO_2H]^{2+}$ which contains a new O-H bond.[15]

We recently reported the synthesis of a variety of lithium-functionalized, pentavalent uranyl Pacman complexes that result from either direct reduction of the hexavalent, uranyl Pacman complex **1** (Scheme 1) or by a C-H activation process.[3] The ready availability of the thermally-stable, doubly-lithiated pentavalent uranyl complex **2** has now allowed us to probe reactions at the uranyl oxo

groups. Here we describe protonation and silylation reactions of **2** that lead to new, covalently-functionalized uranyl complexes.

The reaction between **2** and two equivalents of HCl in pyridine/diethyl ether resulted in the clean formation of the protonated pentavalent uranyl complex **3** as a poorly soluble yellow-brown solid (Scheme 1). We have, as yet, been unable to crystallize **3** and unequivocally determine its structure in the solid state, but the NMR, IR, and microanalytical data of **3** and its deuteriated analogue ***d2*-3** (formed from the reaction between **2** and DCl) fully support its formulation. The IR spectrum of **3** confirms the retention of the U^V oxidation state with a UO_2 stretch observed at 765 cm^{-1} (*cf.* ν_3 = 908 for **1** and 709 cm^{-1} for **2**).[2] The OH and two NH groups have overlapping absorptions in the range 3378 - 3108 cm^{-1} (Supporting Information, Figure S1) while the NH stretch in **1** is at 3368 cm^{-1}, and in **2** is at 3310 cm^{-1}. The OH/NH absorptions shift on deuteriation to 2478 - 2269 cm^{-1}, in accordance with reduced mass calculated values between 2465 and 2259 cm^{-1}. Complete deuteriation was not observed, and likely indicates that a H/D exchange process operates between the OH and NH protons.



Scheme 1. Synthesis of protonated and silylated pentavalent uranyl Pacman complexes **3** and **4**

The ^{1}H NMR spectrum of **3** reveals the presence of paramagnetically-shifted resonances between +90 and –10 ppm, the number and integrals of which are consistent with the retention of a wedged, Pacman structure in solution of *C*s symmetry (Figure S2). The most strongly paramagnetically

contact-shifted resonance at 86.4 ppm integrates as a single proton and is assigned to the UOH group. The ^{2}H NMR spectrum of ***d*$_2$-3** shows deuterium incorporation at this resonance, and also at 7.3 ppm. This latter resonance is therefore assigned as ND (Figure S3) and is obscured by pyridine solvent in the related ^{1}H NMR spectrum. Complex **3** is remarkably stable, showing no signs of disproportionation or decomposition in solution at room or elevated temperatures by ^{1}H NMR spectroscopy.

To further confirm the pentavalent oxidation state of **3**, the stoichiometric reaction between **3** and trityl chloride was carried out (Equation 1 and Figure S4). The ^{1}H NMR spectrum of the reaction mixture showed a 2:1 ratio of the single-electron oxidized product **1** and Gomberg's dimer, the latter formed as a result of single electron reduction.[16] Furthermore, reaction between **3** and TEMPO cleanly regenerated **1** through H-abstraction, while reaction of **3** with two molar equivalents of $LiN(SiMe_3)_2$ re-formed **2**. It is also clear that **3** is not a monolithiated species as no paramagnetic Li environments are seen in the ^{7}Li NMR spectrum and its reaction with two equivalents of $LiN(SiMe_3)_2$ generates **2** and not the triply-lithiated compound $[Li(py)_3OUO(py)Li_2(py)_2(L)]$ reported by us previously.[3]

(1)

H-atom functionalization of the uranyl oxo group is important to aqueous uranyl chemistry. At high pH, equatorial hydroxide ligands are formed at $[UO_2]^{2+}$ from the five equatorially-bound water ligands. The deprotonation of one equatorial OH group and proton-shuttling to an axial oxo has been suggested as key to the exchange of axial and equatorial O-ligands and suggests the existence of interesting T-shaped UO_3 and *cis*-uranyl cations, which are as yet unobserved uranium geometries.[17, 18] Indeed, the spectroscopic data for **3** and its derivatives may provide insight into the speciation of complex aqueous uranyl oxo-hydroxo mixtures.[19]

Reactions between **3** and the chlorosilanes Me_3SiCl, Bu^tMe_2SiCl, or Ph_2HSiCl in pyridine resulted in the clean formation of the oxo-silylated products **4a**, **4b**, and **4c**, respectively (Scheme 1) and the loss of HCl to the pyridine solvent. To our knowledge, this is the first time that metathesis of a functional group that is covalently bound to the uranyl oxo has been seen. While the direct salt elimination reaction between **2** and a molar equivalent of Me_3SiCl resulted in the possible formation of mono-lithiated **4a** (by ^{1}H NMR spectroscopy), pure samples could not be isolated due to the presence of other, as yet unidentified paramagnetic complexes. As with **3**, the ^{1}H NMR spectrum of **4a** shows the

presence of paramagnetically-shifted resonances between +60 and –10 ppm, the number and integrals of which are consistent with a wedged, Pacman structure in solution (Figure S5). Significantly, the resonance at 86.4 ppm, assigned as the OH proton in **3**, is absent in **4a**. Furthermore, a single resonance for the $SiMe_3$ protons is seen at 15.0 ppm and the NH resonance has shifted from 7.3 in **3** to 58.1 ppm in **4a**. In the $^tBuSiMe_2$-functionalized analogue **4b**, the $SiMe_2$ and NH protons resonate at 14.8 and 56.6 ppm, respectively, while the SiH and NH protons in **4c** appear at 37.2 and 54.1 ppm (Figures S6, S7). To confirm the assignment of the NH protons in **4a**, the reaction between ***d*$_2$-3** and Me_3SiCl was carried out and formed ***d*$_2$-4a** which displayed a resonance at 58 ppm in the ^2H NMR spectrum (Figure S8). In the IR spectra of **4a-c** (Figures S9, S10), U=O stretches in **4a-c** are found between 860-823 cm^{-1} and *ca*. 700 cm^{-1}, respectively,[2] whilst the NH stretches are seen at *ca*. 3290 cm^{-1}. In order to confirm the gross structure and O-Si bond formation, crystals of **4a** and **4b** were grown and their solid state structures determined by X-ray crystallography (Figure 1). The X-ray data for **4b** showed problems consistent with multiple twinning. As such, only the connectivity was established (Figure S11), but it is clear from these data that **4a** and **4b** have the same core structure.

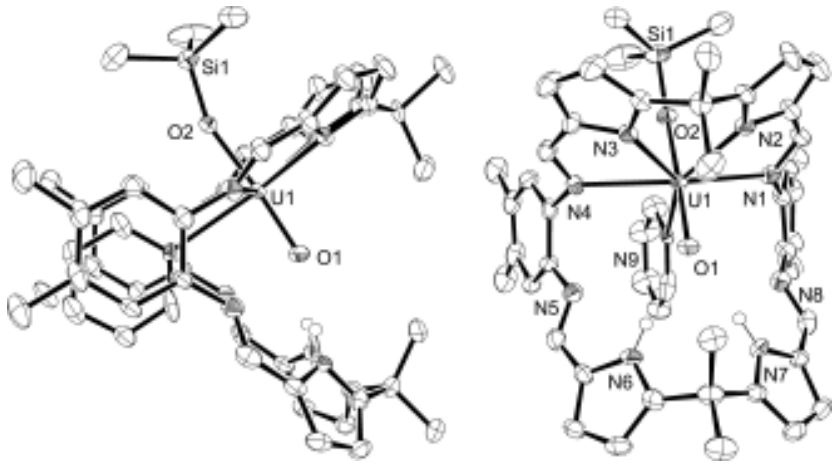


Figure 1. X-ray crystal structure of the trimethylsilylated pentavalent uranyl complex **4a**. For clarity, all hydrogen atoms except those involved in hydrogen bonding and solvent of crystallization are omitted (displacement ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (^{o}): U1-O1 1.854(4); U1-O2 2.034(4); Si1-O2 1.667(5), N6···O1 3.043(6); N7···O1 3.037(6); O1-U1-O2 176.00(19); U1-O2-Si1 160.2(3)

In the structure of **4a** the uranium adopts a distorted pentagonal bipyramidal geometry in which the oxygen ligands are linear and co-axial and the five equatorial sites are made up from the N_4-donor set of the macrocycle and a molecule of pyridine, sandwiched between the two macrocyclic aryl hinges.

The vacant, lower macrocyclic N_4-donor compartment is oriented such that hydrogen bonds are evident between the pyrrole NH groups and the endogenous uranyl oxo group; the N···O separations are slightly shorter in **4a** than in the analogous U^{VI} complex **1** (N···O 3.078(3)/3.103(3) Å). It is clear from the structure that silylation has occurred and that the pentavalent uranium oxidation state is retained. The silylated oxo-uranium bond distance U1-O2 2.034(4) Å and the endogenous U1-O1 distance 1.854(4) are similar to those seen in related uranyl siloxides and are consistent with the pentavalent oxidation state (1.97 to 2.04 Å);[2, 6, 11, 13] in contrast, U(IV) and (III) siloxide bonds are significantly longer (2.06 to 2.20 Å).[20]

In summary, we have shown that it is possible to carry out new OH and OSi bond-forming reactions and interconversions from a pentavalent uranyl complex without the occurrence of deleterious redox processes such as disproportionation. Work is also in progress to identify whether modification of the fifth equatorial solvent site in **3** will enable us to identify possible adducts of **3** and **4** that can help better define uranyl oxo-ion exchange processes.

Experimental Section

Synthetic procedures and characterizing data

3: To a solution of **2** (250 mg, 0.21 mmol) in pyridine was added 1.9 equivalents of HCl in Et_2O (2.0 mL, 0.4 mmol). The resulting suspension was stirred for 2 h, after which the precipitate was isolated and dried under vacuum, to afford 152 mg, 71% of **3** as a brown-yellow solid. Analysis. Found: C, 56.19; H, 4.93; N, 12.56 %. $C_{47}H_{46}N_9O_2Li_2U$ requires C, 55.95; H, 4.80; N, 12.49 % IR (Nujol mull, cm^{-1}): □ 3376, 3189, 1623, 1600, 1583, 1288, 1265, 1218, 1103, 1045, 1020, 892, 782, 765 (UO stretch), 725, 709; ^{1}H NMR (pyridine-d_5): □$_H$ 86.39 (s, 1H), 32.47 (s, 3H), 13.94 (s, 2H), 10.73 (s, 3H + 2H), 5.66 (s, 2H), 3.30 (s, 3H), 2.05 (s, 2H), 1.74 (s, 2H), 0.49 (s, 6H), -1.89 (s, 2H), -2.39 (s, 6H), -2.56 (s, 2H), -3.67 (s, 2H), 7.01 (s, 3H), -8.75 (s, 2H) ppm.

4a-c: To a solution of **3** in pyridine was added neat silyl chloride. The mixture was stirred for 2 h after which the suspension was filtered and the volatiles evaporated from the filtrate to afford silylated **4a-c** as brown-yellow solids.

4a: 3 (75 mg, 0.074 mmol), Me_3SiCl (9.4 µL, 0.074 mmol), Yield 63 mg, 78 %. Analysis. Found: C, 53.28; H, 4.79; N, 11.93 %. $C_{50}H_{56}N_9O_2SiU$ requires C, 55.55; H, 5.22; N, 11.66 %. (MEDAC Ltd, duplicate); IR (Nujol, cm^{-1}): □ 3286 (NH), 1621, 1602, 1583, 1284, 1263, 1216, 1186, 1045, 1033, 1016, 894, 860 (UO stretch), 802, 781, 767, 744, 703 (UO stretch); ^{1}H NMR (pyridine-d_5): □$_H$ 58.10 (s, 2H), 15.02 (s, 9H), 14.58 (s, 3H), 11.13 (s, 2H), 10.04 (s, 2H), 8.63 (s, 2H), 6.65 (s, 3H), 3.60 (s,

2x2H), 3.19 (s, 2H), 2.48 (s, 2H), 1.87(s, 2H), 0.14 (s, 6H), -0.46, (s, 6H), -2.95 (s, 3H), -8.40 (s, 3H) ppm.

4b: 3 (100 mg, 0.09 mmol), $^{t}BuMe_2SiCl$ (14.9 mg, 0.09 mmol), Yield 70 mg, 63 %. Analysis. Found: C, 56.06; H, 5.69; N, 9.90 %. $C_{53}H_{62}N_9O_2SiU$ requires C, 56.67; H, 5.56; N, 11.22 % (MEDAC Ltd, duplicate); IR (Nujol, cm^{-1}): □ 3290 (NH), 1622, 1583, 1282, 1263, 1217, 1182, 1047, 1020, 893, 831 (UO stretch), 769, 725, 694 (UO stretch); ^1H NMR (pyridine-d_5): □$_H$ 56.56 (s, 2H), 14.79 (s, 6H), 13.33 (s, 3H), 11.00 (s, 2H), 10.09 (s, 2H), 9.23 (s, 9H), 9.01 (s, 2H), 6.26 (s, 3H), 3.60 (s, 2 x 2H), 2.98 (s, 2H), 1.28 (s, 2H), 1.09 (s, 2H), -0.16 (s, 6H), -0.38 (s, 6H), -2.80 (s, 3H), -8.59 (s, 3H) ppm.

4c: 3 (75 mg, 0.074 mmol), Ph_2HSiCl (14.6 μL, 0.074 mmol), 60 mg, Yield 67 %. IR (Nujol, cm^{-1}): □ 3291, 2142 (Si-H), 1619, 1600, 1583, 1282, 1261, 1218, 1184, 1118 (Si-Ph), 1047, 1022, 894, 823 (UO stretch), 771, 734, 700 (UO stretch); ^1H NMR (pyridine-d_5): □$_H$ 54.13 (s, 2H, NH), 37.21 (s, 1H, SiH), 17.65 (m, 4H, PhSi), 12.79 (s, 3H), 10.70 (s, 2H), 9.87 (m, 4H, SiPh), 9.79 (s, 2H), 9.15 (m, 2H, SiPh), 8.67 (s, 2H), 6.04 (s, 3H), 4.35 (s, 2H), 3.91 (s, 2H), 3.51 (s, 4H), 1.49 (s, 2H), 0.10 (s, 6H), -0.25 (s, 6H), -2.44 (s, 3H), -8.28 (s, 3H) ppm.

Reaction between 3 and Ph_3CCl: Pyridine was added to a mixture of **3** (25 mg, 0.02 mmol) and trityl chloride (6.1 mg, 0.02 mmol) in a Teflon-tapped NMR tube at room temperature. After a few minutes the solution was dark brown. The reaction mixture was analyzed by ^1H NMR spectroscopy from which it was evident that Gomberg's dimer $Ph_2C=(C_6H_5)CPh_3$ and $UO_2(py)(H_2L)$ **1** had formed in a 0.5:1.0 ratio.

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